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# [12] Application and Public Explanation for Patent for Invention

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[54] Name of Invention: Propylene Ammonia Oxidizing Catalyst

[57] Summary

This invention involves a fluidized bed catalyst for propylene ammonia oxidation and contains a combination of silicon dioxide carriers and a chemical formula as follows:

$A_a B_b C_c Na_d Sr_e Fe_f (Bi_{1-g} Ce_g)_h Mo_{12} O_x$ $

In the formula, A is one or multiple elements selected from lithium, potassium, rubidium, and cesium; B is at least one element selected from magnesium and zinc; C is one or multiple elements selected from nickel, cobalt, manganese, chromium, antimony, phosphorus, boron, tungsten, and vanadium. Characteristics of this catalyst include the ability to adapt to operations under conditions of high pressure and high load, as well as having high acrylonitrile catch rate. It can be used in industrial manufacturing.

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# Rights Claiming Document

1. A propylene ammonia oxidizing catalyst contains a combination of silicon dioxide carriers and a chemical formula as follows:

   $A_a B_b C_c Na_d Sr_e Fe_f (Bi_{1-g} Ce_g)_h Mo_{12} O_x$

   In the formula:

   A is at least one element selected from lithium, potassium, rubidium, and cesium;
   B is at least one element selected from magnesium and zinc;
   C is one or multiple elements selected from nickel, cobalt, manganese, chromium, antimony, phosphorus, boron, tungsten, and vanadium.

   *a*, *b*, *c*, *d*, *e*, and *f* are a ratio of A, B, C, sodium, strontium, and 12 molybdenum atoms; *g* is a ratio between the cerium atoms and the sum of and bismuth and cerium atoms; *h* is a ratio between the sum of bismuth and cerium atoms and the 12 molybdenum atoms;

   Of these:

   *a* has a value of 0.001 ~ 0.7;
   *b* has a value of 0 ~ 3;
   *c* has a value of 0.1 ~ 10;
   *d* has a value of 0.1 ~ 0.7, conditional on the sum of the value of *a* and the value of *d* being between 0.1 ~ 1.0;
   *e* and *f* both have values of 0.01 ~ 4;
   *g* has a value of 0.3 ~ 0.8;
   *h* has a value of 0.5 ~ 2;
   *x* has a value of the total sum needed to satisfy the other elements' chemical valence requirement for oxygen atoms;

   The silicon dioxide carrier content in the catalyst has a weight percentage of 30 ~ 70%.

2. According to the propylene ammonia oxidizing catalyst listed in Right Claim 1, its special characteristic is that the sum of the values of *a* and *d* is 0.2 ~ 0.7.
3. According to the propylene ammonia oxidizing catalyst listed in Right Claim 1, its special characteristic is that the values of *e* and *f* are 0.01 ~ 2.5 and 0.5 ~ 3 respectively.
4. According to the propylene ammonia oxidizing catalyst listed in Right Claim 1, its special characteristic is that the value of *h* is 0.7 ~ 2.
5. According to the propylene ammonia oxidizing catalyst listed in Right Claim 1, its special characteristic is that the weight percentage of the silicon dioxide carrier content in the catalyst is 40 ~ 60%.

# Explanation

## Propylene Ammonia Oxidizing Catalyst

This invention involves a fluidized bed catalyst for propylene ammonia oxidation, regarding in particular the propylene ammonia oxidizing acrylonitrile fluidized bed catalyst containing strontium and cerium.

Acrylonitrile is an important organic raw material of the chemical industry that is produced through a propylene ammonia oxidation reaction. In order to obtain a highly active and highly selective fluidized bed catalyst, a series of advances have been made through continuous exploration. For the most part, these advances involve the catalytic activity portion and emphasize the components of catalytic activity so as to increase the activity and selectivity of the catalyst, thereby raising the single pass catch rate of the acrylonitrile and increasing the production load.

That acrylonitrile catalysts can be used under conditions of high propylene load and high reaction pressure while achieving a high level of reaction capability in acrylonitrile production devices is the objective that has always been pursued in industrial production of acrylonitrile. Conditions of high load and high reaction pressure can raise acrylonitrile yield and the processing capability of the reactor. Catalysts that withstand high loads can reduce catalyst load weight and extend the capability of the reactor in production devices of a certain scale. In this way, factories can appropriately raise production capability in accordance with the needs of the market. Catalysts that withstand high pressure can also satisfy environmental requirements that are increasing daily. The absorption tower inputs air waste at a dependable tower top pressure directly into the furnace for combustion and thereby reduces the air pollution rendered when direct air input is not done.

High load and high pressure are an indication of increased concentration of propylene, ammonia, and oxygen reactants in the reaction air. It requires that the catalyst have the capability to handle even more reactants during the unit time, and the reactive capability of the acrylonitrile catalyst under conditions of high load and high pressure therefore actually reflects the level of activity and selectivity of the catalyst. This has put forward even higher requirements for the catalyst's own synthesis.

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A propylene ammonia oxidation for the manufacture of acrylonitrile was introduced in Document US4228098. The catalyst used in this industry uses molybdenum -- bismuth -- iron -- sodium -- phosphorus as the principal active components. The chromium element is not a component of its catalyst, and when bismuth and iron are emphasized in the catalyst at a certain proportional relationship, the catalyst has the capability to develop into a better composite. The published catalyst testing conditions in this technology are catalyst propylene load (WWH) of 0.050 hours$^{-1}$ in the fluid bed reactor, reaction pressure of 0.05 MPa, and acrylonitrile maximum unit catch of 80.9%. The catalyst test data under conditions of high load and high reaction pressure have not been published, but it can be seen from the data that was published that, in an unchanged circumstances and under all other reaction conditions, the acrylonitrile unit catch when the reaction pressure is 0.05 MPa is 5% lower than the test data under ordinary pressure. The following shortcomings exist in this document: On the one hand, it lacks data under conditions of high propylene load and high reaction pressure, so the production capability for this type of device is relatively low; on the other hand, the single pass catch rate for acrylonitrile is also low. Documents JP 7-289901 and JP 7-328441 have introduced a Mo-Bi-Ce-Fe-Co system acrylonitrile fluidized bed catalyst and a Mo-Bi-Ce-Fe-Ni system acrylonitrile fluidized bed catalyst, respectively. The corresponding relationship between the bismuth and cerium element components has been stipulated in these two documents, and it is believed that use of this ammonia oxidized catalyst combination not only can capture a high acrylonitrile production rate, it can effectively prevent reduced production rate of acrylonitrile as well even though there is an extended reaction time for this production process. The catalyst test conditions published in this document are a catalyst load of 1000 ~ 2000 grams in the fluidized bed reactor, reaction pressure of 0.5 kg/cm$^2$, reaction temperature of 430 ~ 440°C, and contact time of 5 ~ 7 seconds. Calculations show that the catalyst propylene load (WWH) is ~ 0.050 hours$^{-1}$ with a maximum acrylonitrile unit catch of 82.0% in this time,

but neither document published catalyst test data under conditions of high propylene load and high reaction pressure. For this reason, it is very difficult to explain the operating capability of this catalyst under conditions of high pressure and high load. Document JP 7-303836 has introduced a Mo-Bi-Ce-Fe-Zn system acrylonitrile catalyst. The catalyst test conditions in this document are an internal diameter of 1 cm, reaction pressure of 0.5 $kg/cm^2$, reaction temperature of 430°C, catalyst load of 60 grams in the reactor, and contact time of 6.0 seconds. Calculations show that the propylene load (WWH) is 0.042 $hours^{-1}$ with a maximum acrylonitrile catch rate of 80.0% in this time. This document likewise does not touch on data for high pressure and high load operating conditions, and it is therefore also very difficult to explain the operating capability of this catalyst under conditions of high pressure and high load.

It is the objective of this invention to overcome the shortcomings in the documents cited above regarding catalysts not involving high pressure and high load operations and to provide a new propylene ammonia oxidizing fluidized bed catalyst. This catalyst is suited to operation under high reaction pressure and high load and can also maintain a high acrylonitrile single pass catch rate.

The objective of this invention was brought about through the following technological schemes: A propylene ammonia oxidizing catalyst containing silicon dioxide carriers and a chemical formula as follows:

$A_a\, B_b\, C_c\, Na_d\, Sr_e\, Fe_f\, (Bi_{1-g}\, Ce_g)_h\, Mo_{12}\, O_x$

In the formula:

A is one or multiple elements selected from lithium, potassium, rubidium, and cesium;
B is at least one element selected from magnesium and zinc;
C is one or multiple elements selected from nickel, cobalt, manganese, chromium, antimony, phosphorus, boron, tungsten, and vanadium.

*a, b, c, d, e,* and *f* are a ratio of A, B, C, sodium, strontium, and 12 molybdenum atoms; *g* is a ratio of cerium atoms and a sum of bismuth and cerium atoms; *h* is a ratio of a sum of bismuth and cerium atoms and the 12 molybdenum atoms;

Of these:

*a* has a value of 0.001 ~ 0.7;
*b* has a value of 0 ~ 3;
*c* has a value of 0.1 ~ 10;
*d* has a value of 0.1 ~ 0.7, conditional on the sum of the value of *a* and the value of *d* being between 0.1 ~ 1.0;
*e* and *f* both have values of 0.01 ~ 4;
*g* has a value of 0.3 ~ 0.8;
*h* has a value of 0.5 ~ 2;
*x* has a value of the total sum needed to satisfy the other elements' requirement for oxygen atoms;

The silicon dioxide carrier content in the catalyst has a weight percentage of 30 ~ 70%.

In the technological scheme above, the preferential range for the sum of the values of *a* and *d* is 0.2 ~ 0.7; the preferential range for the values of *e* and *f* are 0.01 ~ 2.5 and 0.5 ~ 3, respectively; the preferential range for the value of *h* is 0.7 ~ 2; the preferential weight proportion range of the silicon dioxide carrier content in the catalyst is 40 ~ 60%.

In this invention, the use of cerium in place of a portion of the bismuth can increase the product catch rate and catalyst stability. Use of the strongly alkaline earth metal strontium in place of a portion of the alkali metals, in particular potassium or other alkaline earth metals, can on the one hand further strengthen the activity of the catalyst while at the same time helping to lower excessive carbon dioxide in production. Use of the elements magnesium or zinc can enable more even distribution of the destination

product following the catalytic reaction -- i.e., the resulting amount of carbon monoxide and carbon dioxide are effectively reduced. The coordinating effects of each of the catalyst components have rendered the catalyst good capability, enabling it to operate under conditions of reaction pressure of 0.14 MPa, reaction temperature of 440°C, and propylene load (WWH) of 0.085 hours$^{-1}$. Moreover, the single pass catch rate for its destination product of acrylonitrile can still achieve a maximum of 79.5% which is suitable for operations under conditions of high pressure and high load. Excellent results have been achieved.

The manufacturing method of the catalyst in this invention can be carried out in accordance with regular practices. First, each of the catalyst's components are mixed with the carrier and water into a pulp followed by molding it into micro granules by spray drying. Finally, it is baked to create the catalyst. An aqueous solution of each of the components of the pulp compound and the carrier is made in accordance with the method outlined in China Patent 87103455.7 (CN1005248B).

The raw materials used for each of the catalyst's components in this invention are as follows:

It is best to use its nitrate, hydroxide, or decomposable salt oxide for the elements in types A and B.

It is best to use the corresponding acid or its ammonium salt for the phosphorus, boron, tungsten, and vanadium element components in type C. Halides and antimony solutions of diantimony trioxide, diantimony pentoxide, and hydrolytically created antimony oxide can be used for the antimony. Its oxide or salt decomposed into an oxide can be used for the rest. It is best if the salt used is a water soluble nitrate.

It is best to use chromium trioxide (hexavalence chromium), chromium nitrate or a secondary mixture.

Sodium nitrate, sodium hydroxide, sodium silicate, or any other decomposable sodium compound can be used for the sodium component.

The element's oxide salt or decomposed oxide salt can be used for the iron, bismuth, cerium, and strontium components. It is best if the salt used is a water soluble nitrate.

Molybdenum oxide or neodymium molybdate can be used for the molybdenum component.

The catalyst activity testing for this invention is carried out in a fluidized bed reactor with an internal diameter of 38 mm. The catalyst load capacity is 400 g, reaction temperature ~~is 440°C,~~ reaction pressure is 0.14 MPa, raw material distribution proportion (mole) is ammonia: air = 1: 1.2: 9.8, and the catalyst propylene load (WWH) is 0.085 hours$^{-1}$.

The definitions of propylene transformation rate, acrylonitrile selectivity, and single pass catch rate in this invention are as follows:

$$\text{Propylene Transformation Rate (\%)} = \frac{\text{Propylene Mole Number of Reaction}}{\text{Propylene Feed Mole Number}} \times 100$$

$$\text{Acrylonitrile Selectivity (\%)} = \frac{\text{Mole Number of Acrylonitrile Produced}}{\text{Propylene Mole Number of Reaction}} \times 100$$

Single Pass Catch Rate (%) = $\dfrac{\text{Mole Number of Acrylonitrile Produced}}{\phantom{x}}$ x 100

Propylene Feed Mole Number

Further explanation of this invention is given through the following examples:

[Example 1]

Substance (A) results from mixing 1.8 g cesium nitrate, 2.4 g sodium nitrate, and 5.9 g strontium nitrate, adding 30 g water and dissolving over heat; substance (B) results from dissolving 8.4 g chromium trioxide in 8.4 g water; substance (C) results from dissolving 19.4 g ammonium tungstate in 100 ml aqueous ammonia of 5% concentration, dissolving 395.2 g neodymium molybdate in 325 g hot water at 50 ~ 90°C and combining the two solutions; material (D) results from mixing 40.7 g bismuth nitrate, 36.5 g cerium nitrate, 90.9 g magnesium nitrate, 282.1 g nickel nitrate, and 135.7 g iron nitrate, adding 70 g water and dissolving over heat.

Combine substance (A) and 1,250 g of 40% concentration silica sol, add substances (B), (C), and (D) under agitation, and completely agitate until it is a pulp. Spray dry the resulting pulp in accordance with regular methods to form micro granules. Finally, bake in a revolving baking oven with internal diameter of 89 mm and length of 1700 mm (Φ 89 x 1700 mm) at 610°C for 1 hour. The composition of the catalyst made is: 50% $Cs_{0.05}\ Mg_{1.9}\ Ni_{5.2}\ Cr_{0.45}\ W_{0.45}\ Na_{0.15}\ Sr_{0.15}\ Fe_{1.8}\ Bi_{0.45}\ Ce_{0.45}\ Mo_{12}\ O_x$ + 50% $Si\ O_2$.

[Examples 2 ~ 9 and Comparative Examples 1 ~ 3]

Use the same basic method as in Example 1 to prepare a catalyst with the differing components listed below. Carry out propylene ammonia oxidation to produce acrylonitrile using the catalyst produced under the following reaction conditions. See Table 1 for results.

The reaction conditions of the above examples and comparative examples are:

Φ 38 mm fluidized bed reactor
Reaction temperature 440°C
Reaction pressure 0.14 MPa
Catalyst load capacity 400 g
Catalyst propylene load (WWH) 0.085 hours$^{-1}$
Raw material distribution proportion (mole) $C_3$ / $NH_3$ / air = 1 / 1.2 / 9.8

Table 1

| Example No. | Catalyst Composition | g | h | Single pass catch rate | | | AN Selectivity % | $C_3$ Transformation Rate % |
|---|---|---|---|---|---|---|---|---|
| | | | | AN | CO | $CO_2$ | | |
| Example 1 | 50% $Cs_{0.05}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_2$ | 0.50 | 0.90 | 79.2 | 3.8 | 7.0 | 80.7 | 98.1 |
| Example 2 | 50% $Cs_{0.05}K_{0.05}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_2$ + 50% $SiO_2$ | 0.50 | 0.90 | 78.2 | 3.7 | 7.7 | 79.9 | 97.9 |
| Example 3 | 50% $Cs_{0.07}Mg_{2.1}Ni_{5.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.9}Mo_{12}O_2$ + 50% $SiO_2$ | 0.67 | 1.35 | 79.5 | 4.0 | 6.9 | 80.7 | 98.5 |
| Example 4 | 50% $Cs_{0.07}Mg_{2.1}Ni_{5.0}Cr_{0.45}Mn_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.9}Mo_{12}O_2$ + 50% $SiO_2$ | 0.67 | 1.35 | 78.5 | 4.1 | 7.5 | 79.6 | 98.6 |
| Example 5 | 50% $Cs_{0.07}Zn_{2.1}Ni_{5.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.9}Mo_{12}O_2$ + 50% $SiO_2$ | 0.67 | 1.35 | 79.0 | 3.8 | 7.2 | 80.4 | 98.3 |
| Example 6 | 50% $Cs_{0.07}Mg_{2.1}Ni_{5.0}Cr_{0.45}P_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.25}Ce_{0.5}Mo_{12}O_2$ + 50% $SiO_2$ | 0.67 | 0.75 | 79.4 | 4.0 | 6.5 | 81.0 | 98.0 |
| Example 7 | 50% $Cs_{0.07}Zn_{2.1}Ni_{2.0}Co_{2.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_2$ + 50% $SiO_2$ | 0.59 | 1.10 | 78.8 | 4.2 | 7.0 | 80.3 | 98.1 |
| Example 8 | 50% $Cs_{0.09}K_{0.05}Mg_{2.0}Ni_{5.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.07}Fe_{1.8}Bi_{0.5}Ce_{0.45}Mo_{12}O_2$ + 50% $SiO_2$ | 0.47 | 0.95 | 78.2 | 3.8 | 7.8 | 79.5 | 98.4 |
| Example 9 | 50% $Cs_{0.09}Mg_{2.1}Ni_{4.9}Cr_{0.45}Mn_{0.45}W_{0.25}Na_{0.15}Sr_{0.1}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_2$ + 50% $SiO_2$ | 0.59 | 1.10 | 79.3 | 3.8 | 6.9 | 80.7 | 98.3 |
| Comparative Example 1 | 50% $Cs_{0.05}K_{0.15}Mg_{1.9}Ni_{6.2}Cr_{0.45}W_{0.45}Na_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_2$ + 50% $SiO_2$ | 0.50 | 0.90 | 77.3 | 3.5 | 8.7 | 79.3 | 97.5 |
| Comparative Example 2 | 50% $Cs_{0.05}K_{0.05}Mg_{1.9}Ni_{6.2}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.9}Mo_{12}O_2$ + 50% $SiO_2$ | 0 | 0.90 | 77.0 | 4.0 | 8.9 | 78.5 | 98.1 |
| Comparative Example 3 | 50% $K_{0.2}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_2$ + 50% $SiO_2$ | 0.50 | 0.90 | 76.5 | 4.3 | 9.5 | 78.5 | 97.5 |

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[54]发明名称 丙烯氨氧化催化剂

[57]摘要

本发明涉及一种丙烯氨氧化的流化床催化剂，含有二氧化硅载体和化学式如下 的组合物组成：

$A_aB_bC_cNa_dSr_eFe_f(Bi_{1-g}Ce_g)_hMo_{12}O_x$ $ 式中A为选自锂、钾、铷、铯中的一种或多种元素；B为选自镁、锌中的至少 一种元素；C为选自镍、钴、锰、铬、锑、磷、硼、钨、钒中的一种或多种元 素。该催化剂具有能适应高压、高负荷操作，同时具有高丙烯腈收率的特点，可用于工业生产中。

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# 权利要求书

1、一种丙烯氨氧化催化剂，含有二氧化硅载体和化学式如下的组合物组成：

$A_aB_bC_cNa_dSr_eFe_f(Bi_{1-g}Ce_g)_hMo_{12}O_x$

式中A为选自锂、钾、铷、铯中的一种或多种元素；

B为选自镁、锌中的至少一种元素；

C为选自镍、钴、锰、铬、锑、磷、硼、钨、钒中的一种或多种元素；

a、b、c、d、e、f分别为A、B、C、钠、锶、铁与12个钼原子之比，g为铈原子与铋和铈原子之和之比，h为铋和铈原子之和与12个钼原子之比；

其中：a值为0.001～0.7；

b值为0～3；

c值为0.1～10；

d值为0.1～0.7，条件是a值和d值之和为0.1～1.0；

e值、f值均为0.01～4；

g值为0.3～0.8；

h值为0.5～2；

x值为满足其它元素化合价所需氧原子数的总和；

催化剂中载体二氧化硅含量以重量百分比计为30～70%。

2、根据权利要求1所述丙烯氨氧化催化剂，其特征在于a值和d值之和为0.2～0.7。

3、根据权利要求1所述丙烯氨氧化催化剂，其特征在于e值、f值分别为0.01～2.5、0.5～3。

4、根据权利要求1所述丙烯氨氧化催化剂，其特征在于h值为0.7～2。

5、根据权利要求1所述丙烯氨氧化催化剂，其特征在于催化剂中载体二氧化硅含量以重量百分比计为40～60%。

# 丙烯氨氧化催化剂

本发明涉及丙烯氨氧化流化床催化剂，尤其是关于含锶、铈的丙烯氨氧化制丙烯腈流化床催化剂。

丙烯腈是重要的有机化工原料，它是通过丙烯氨氧化反应生产的。为获得高活性、高选择性的流化床催化剂，人们经过不断探索，进行了一系列改进。这些改进大都涉及催化剂活性部份，注重催化剂活性组份之间的搭配，来提高催化剂的活性与选择性，从而达到丙烯腈单程收率的提高，以及生产负荷的提高。

在丙烯腈生产装置中，希望丙烯腈催化剂能够在高丙烯负荷、高反应压力条件下使用，并达到高水平的反应性能，一直是丙烯腈工业生产中人们追求的目标。高负荷、高压反应条件可以提高丙烯腈产量和反应器的处理能力。耐高负荷催化剂对一定规模的生产装置而言，可减少催化剂装填量，并可使反应器扩能，这样工厂可以根据市场需求适当提高生产能力；耐高压催化剂可以满足日益提高的环保要求，吸收塔放空废气可依靠塔顶压力直接送入炉中燃烧，减少不经处理直接放空带来的空气污染。

高负荷、高压意味着反应气氛中反应物丙烯、氨和氧的浓度增加，它要求催化剂必须具备在单位时间内处理更多反应物的能力，因此丙烯腈催化剂在高负荷、高压条件下的反应性能，其实质是反映了催化剂活性和选择性的高低，对催化剂本身的综合性能提出了更高的要求。

文献 US4228098 中介绍了一种丙烯氨氧化生产丙烯腈工艺，其工艺中所用催化剂是以钼—铋—铁—钠—磷为主要活性组份，其催化剂组成中不含有铬元素，强调铋与铁在催化剂中保持一定的比例关系时，催化剂能发挥出较好的综合性能。该工艺中公开的催化剂考评条件为流化床反应器中催化剂丙烯负荷(WWH) 为 0.050 小时$^{-1}$、反应压力为 0.05MPa，此时丙烯腈单收最高为 80.9%，没有公开在高丙烯负荷、高反应压力条件下催化剂的考评数据，但从公开的数据中可以看出，在其它反应条件不变的情况下，反应压力 0.05MPa 时的丙烯腈单收比常压下的考评数据低近 5%。该文献存在以下缺点：一方面缺少高丙烯负荷、高反应压力条件下的数据，这样装置的生产能力较低；另一方面丙烯腈的单程收率也不高。文献 JP 平 7-289901 和 JP 平 7-328441 中分别介绍了一种 Mo-Bi-Ce-Fe-Co 体系的丙

烯腈流化床催化剂和 Mo-Bi-Ce-Fe-Ni 体系的丙烯腈流化床催化剂。该两份文献中规定了催化剂组成元素中铋与铈的对应关系，认为使用这种氨氧化催化剂组合物不仅能获得高产率的丙烯腈，而且即使在该生产过程延长反应时间也能有效地防止丙烯腈产率的降低。文献中公开的催化剂考评条件为流化床反应器中催化剂装填量 1000 ～ 2000 克、反应压力 $0.5kg/cm^2$、反应温度 430 ～ 440 ℃、接触时间 5 ～ 7 秒，由计算可知催化剂丙烯负荷(WWH)为～ 0.050 小时$^{-1}$，此时丙烯腈单收最高为 82.0%，但它们均没有公开在高丙烯负荷、高反应压力条件下催化剂的考评数据，因此很难说明该催化剂在高压、高负荷条件下的操作性能。文献 JP 平 7-303836 中介绍了 Mo-Bi-Ce-Fe-Zn 体系的丙烯腈催化剂。该文献的催化剂考评条件为内径为 1 厘米，反应压力为 $0.5kg/cm^2$，反应温度 430 ℃，反应器中催化剂装填量为 60 克，接触时间 6.0 秒，经计算丙烯负荷(WWH)为 0.042 小时$^{-1}$，此时丙烯腈单收最高为 80.0%。在该文献中同样没有涉及高压、高负荷操作条件的数据，因此也很难说明该催化剂在高压、高负荷条件下的操作性能。

本发明的目的是为了克服上述文献中催化剂不涉及高压、高负荷操作的缺点，提供一种新的丙烯氨氧化流化床催化剂，该催化剂适合于高反应压力、高丙烯负荷下操作，且同时能保持高的丙烯腈单程收率。

本发明的目的是通过以下的技术方案来实现的：一种丙烯氨氧化催化剂，含有二氧化硅载体和化学式如下的组合物组成：

$A_aB_bC_cNa_dSr_eFe_f(Bi_{1-g}Ce_g)_hMo_{12}O_x$

式中 A 为选自锂、钾、铷、铯中的一种或多种元素；

B 为选自镁、锌中的至少一种元素；

C 为选自镍、钴、锰、铬、锑、磷、硼、钨、钒中的一种或多种元素；

a、 b 、 c 、 d 、 e 、 f 分别为 A 、 B 、 C 、钠、锶、铁与 12 个钼原子之比，

g 为铈原子与铋和铈原子之和之比， h 为铋和铈原子之和与 12 个钼原子之比；

其中： a 值为 0.001 ～ 0.7 ；

b 值为 0 ～ 3 ；

c 值为 0.1 ～ 10 ；

d 值为 0.1 ～ 0.7 ，条件是 a 值和 d 值之和为 0.1 ～ 1.0 ；

e 值、 f 值为 0.01 ～ 4 ；

g 值为 0.3 ～ 0.8 ；

h 值为 0.5 ～ 2；

x 值为满足其它元素化合价所需氧原子数的总和：

催化剂中载体二氧化硅含量以重量百分比计为 30 ～ 70%。

上述技术方案中 a 值和 d 值之和的优选范围为 0.2 ～ 0.7； e 值、 f 值的优选范围分别为 0.01 ～ 2.5 、 0.5 ～ 3； h 值的优选范围为 0.7 ～ 2；催化剂中载体二氧化硅含量以重量百分比计优选范围为 40 ～ 60%。

在本发明中用铈取代一部分铋可提高催化剂的产物收率和稳定性，用强碱性的碱土金属锶取代一部分的碱金属，尤其是钾或其它碱土金属，一方面可进一步增强催化剂的活性，同时有利于降低产生过多的二氧化碳，使用镁或锌元素可使催化反应后，目的产物的分布更趋合理，即产物一氧化碳、二氧化碳的生成量有效降低等。催化剂中各组份的协同作用，赋予了催化剂较好的性能，使催化剂在反应压力 0.14MPa ，反应温度 440 ℃，丙烯负荷(WWH)为 0.085 小时$^{-1}$ 条件下操作，其目的产物丙烯腈的单程收率最高仍能达到 79.5%，适合于高压、高负荷条件下操作，取得了很好的效果。

本发明的催化剂制造方法可按常法进行。首先将催化剂各组份与载体和水混合成浆料，经喷雾干燥成型为微球状，最后焙烧制成催化剂。浆料的配制是将催化剂各组份的水溶液和载体按中国专利 87103455.7(CN1005248B)所述的方法进行。

本发明催化剂中各组份所使用的原料为：

组份 A 类、 B 类元素最好用其硝酸盐、氢氧化物或可分解为氧化物的盐类。

组份 C 类元素中的磷、硼、钨、钒最好用其相应的酸类或其铵盐；锑可用三氧化二锑、五氧化二锑、水解生成氧化锑的卤化物及锑溶胶；其它可用其氧化物或分解为氧化物的盐类，所用的盐类最好是水溶性的硝酸盐。

组份铬最好用三氧化铬(六价铬)、硝酸铬或二者的混合物。

组份钠可用硝酸钠、氢氧化钠、硅酸钠或任何可以分解的钠化合物。

组份铁、铋、铈、锶可用其氧化物或分解为氧化物的盐类，所用的盐类最好是水溶性的硝酸盐。

组份钼可用氧化钼或钼酸铵。

本发明催化剂的活性考评是在内径为 38 毫米的流化床反应器中进行的。催化剂装填量 400g，反应温度 440 ℃，反应压力 0.14MPa，原料配比(摩尔)为丙烯：氨：空气＝ 1 ： 1.2 ： 9.8，催化剂的丙烯负荷(WWH)为 0.085 小时$^{-1}$。

在本发明中丙烯转化率、丙烯腈选择性和单程收率的定义如下：

$$丙烯转化率（\%）=\frac{反应的丙烯摩尔数}{丙烯进料摩尔数}\times 100$$

$$丙烯腈选择性（\%）=\frac{生成丙烯腈摩尔数}{反应的丙烯摩尔数}\times 100$$

$$丙烯腈单程收率（\%）=\frac{生成丙烯腈摩尔数}{丙烯进料摩尔数}\times 100$$

下面通过实施例对本发明作进一步的阐述。

【实施例 1】

将 1.8 克硝酸铯、 2.4 克硝酸钠和 5.9 克硝酸锶混合，加水 30 克，加热后溶解，得物料(A)；将 8.4 克三氧化铬溶于 8.4 克水中，得物料(B)；将 19.4 克钨酸铵溶于 100 毫升重量浓度为 5%的氨水中，将 395.2 克钼酸铵溶于 325 克 50 ～ 90 ℃热水中，将两溶液混合得物料(C)；将 40.7 克硝酸铋、 36.5 克硝酸铈、 90.9 克硝酸镁、 282.1 克硝酸镍和 135.7 克硝酸铁混合，加水 70 克，加热后溶解，得物料(D)。

将物料(A)与 1250 克重量浓度为 40 %的硅溶胶混合，在搅拌下加入物料(B)和 (C)和(D)，充分搅拌得浆料，按常法将制成的浆料在喷雾干燥器中成型为微球粒，最后在内径为 89 毫米，长度为 1700 毫米(Φ 89 × 1700mm)的旋转焙烧炉中于 610 ℃焙烧 1 小时，制成的催化剂组成为： $50\%Cs_{0.05}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_x+50\%SiO_2$

【实施例 2 ～ 9 及比较例 1 ～ 3】

采用与实施例 1 基本相同的方法制备具有下表中不同组成的催化剂，并用所制得的催化剂在下面的反应条件下进行丙烯氨氧化生成丙烯腈的反应，结果见表 1 。

上述实施例与比较例的反应条件为：

Φ 38mm 流化床反应器

反应温度　440 ℃

反应压力　0.14MPa

催化剂装填量　400g

催化剂丙烯负荷(WWH)　0.085 小时$^{-1}$

原料配比(摩尔)　$C_3^=/NH_3/$空气＝ 1/1.2/9.8

表 1

| 实施例 | 催 化 剂 组 成 | g | h | 单 程 收 率 % | | | AN 选择性 | $C_3^=$转化率 |
|---|---|---|---|---|---|---|---|---|
| | | | | AN | CO | $CO_2$ | % | % |
| 实施例 1 | $50\%Cs_{0.05}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_x+50\%SiO_2$ | 0.50 | 0.90 | 79.2 | 3.8 | 7.0 | 80.7 | 98.1 |
| 实施例 2 | $50\%Cs_{0.05}K_{0.05}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_x+50\%SiO_2$ | 0.50 | 0.90 | 78.2 | 3.7 | 7.7 | 79.9 | 97.9 |
| 实施例 3 | $50\%Cs_{0.07}Mg_{2.1}Ni_{5.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.9}Mo_{12}O_x+50\%SiO_2$ | 0.67 | 1.35 | 79.5 | 4.0 | 6.9 | 80.7 | 98.5 |
| 实施例 4 | $50\%Cs_{0.07}Mg_{2.1}Ni_{5.0}Cr_{0.45}Mn_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.9}Mo_{12}O_x+50\%SiO_2$ | 0.67 | 1.35 | 78.5 | 4.1 | 7.5 | 79.6 | 98.6 |
| 实施例 5 | $50\%Cs_{0.07}Zn_{2.1}Ni_{5.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.9}Mo_{12}O_x+50\%SiO_2$ | 0.67 | 1.35 | 79.0 | 3.8 | 7.2 | 80.4 | 98.3 |
| 实施例 6 | $50\%Cs_{0.07}Mg_{2.1}Ni_{5.0}Cr_{0.45}P_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.25}Ce_{0.5}Mo_{12}O_x+50\%SiO_2$ | 0.67 | 0.75 | 79.4 | 4.0 | 6.5 | 81.0 | 98.0 |
| 实施例 7 | $50\%Cs_{0.07}Zn_{2.1}Ni_{3.0}Co_{2.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.65}Mo_{12}O_x+50\%SiO_2$ | 0.59 | 1.10 | 78.8 | 4.2 | 7.0 | 80.3 | 98.1 |
| 实施例 8 | $50\%Cs_{0.09}K_{0.05}Mg_{2.0}Ni_{5.0}Cr_{0.45}W_{0.45}Na_{0.15}Sr_{0.07}Fe_{1.8}Bi_{0.5}Ce_{0.45}Mo_{12}O_x+50\%SiO_2$ | 0.47 | 0.95 | 78.2 | 3.8 | 7.8 | 79.5 | 98.4 |
| 实施例 9 | $50\%Cs_{0.09}Mg_{2.1}Ni_{4.8}Cr_{0.45}Mn_{0.45}W_{0.25}Na_{0.15}Sr_{0.1}Fe_{1.8}Bi_{0.45}Ce_{0.65}Mo_{12}O_x+50\%SiO_2$ | 0.59 | 1.10 | 79.3 | 3.8 | 6.9 | 80.7 | 98.3 |
| 比较例 1 | $50\%Cs_{0.05}K_{0.15}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_x+50\%SiO_2$ | 0.50 | 0.90 | 77.3 | 3.5 | 8.7 | 79.3 | 97.5 |
| 比较例 2 | $50\%Cs_{0.05}K_{0.05}Mg_{1.9}Ni_{5.2}Cr_{0.46}W_{0.46}Na_{0.15}Sr_{0.15}Fe_{1.8}Bi_{0.9}Mo_{12}O_x+50\%SiO_2$ | 0 | 0.90 | 77.0 | 4.0 | 8.9 | 78.5 | 98.1 |
| 比较例 3 | $50\%K_{0.2}Mg_{1.9}Ni_{5.2}Cr_{0.45}W_{0.45}Na_{0.15}Fe_{1.8}Bi_{0.45}Ce_{0.45}Mo_{12}O_x+50\%SiO_2$ | 0.50 | 0.90 | 76.5 | 4.3 | 9.5 | 78.5 | 97.5 |